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## ELECTROSTATIC EMISSION OF ELECTRONS FROM SILICON

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## ELECTROSTATIC EMISSION OF ELECTRONS FROM SILICON

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Determination of the volt-ampere characteristics for electrostatic electron emission of silicon. The characteristics, represented graphically, are generally straight lines tending to deflect at high voltages. A desorption technique is used to obtain clean silicon emitter surfaces which permit a qualitative comparison of experimental data with theoretical figures and reduce the probability of boron diffusion. A model of "heating" of the electron gas is used to clarify the behavior of the volt-ampere characteristics at high voltages.

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The electrostatic emission of electrons (EEE) has been studied completely only in the case of metals; various volt-ampere characteristics of emission /62 have been obtained for semiconductors, the course of which is quite difficult to explain chiefly because of uncertainty with regard to the condition of the emitting surface. A study of EEE from semiconductors with careful control of the state of the emitting surface (and, possibly, the layer adjacent to it) will enable one to prove the correctness of the current theories of EEE from semiconductors and to examine the role of surface conditions, the effects of strong fields and so forth.

A great interest in silicon, as the starting material for the semiconductor industry and the production on an industrial scale of monocrystals of silicon with very good control of the electrophysical properties have determined its choice as the object of our investigations.

A characteristic property of silicon, as the object of a study of EEE, is its very great chemical activity and the difficulty of cleaning the surface of oxide film, the melting point of which is higher than the melting point of

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/Numbers in the margin indicate pagination of the original foreign text.

silicon itself. In addition, the extremely insignificant "contamination" of the surface and volume by foreign atoms, combined with the projector technique (completely immaterial for metals), can strongly distort its semiconductor properties. All this creates additional difficulties in the usual projector technique connected with metallic and comparatively inert semiconductor emitters.

D'Azaro [1] first cleansed the monocrystalline surface of silicon of contaminants (mainly, apparently, the mono- and di-oxides of silicon) by heating the point and by simultaneous action on it of an electrical field. The oxide film was "torn off" from the hot point and the pure emission pattern of silicon of chosen orientation was obtained. The volt-ampere curve proved to be linear in the range of currents from  $4 \cdot 10^{-6}$  up to  $2 \cdot 10^{-9}$  A. It was impossible to compare these results with the current theory of EEE from semiconductors of Morgulis-Stratton-Vasil'yev [2-5] since the silicon was of p-type and strongly degenerated because of a large concentration of boron admixtures (up to  $10^{20}$  atoms in  $1 \text{ cm}^3$ ).

Allen et al. [6] showed that the emission pattern of silicon can be obtained only after heating to temperatures of about the melting point without application of a field; in principle, it is possible carry out purification of the silicon surface by high temperature heating thanks to the very high pressure of the saturated vapors of its oxides and to a temperature in the vicinity of the melting point of silicon, although the emitter at such a temperature is /63 very "dulled". The authors obtained emission patterns similar to those obtained in [1]. However, it was impossible to compare the experimental data with the theoretical since, during heating of the silicon to temperatures of about 1550-1600°K, a certain amount of boron fell onto the point from the surface of the

instrument, made of borosilicate glass, and it may have diffused into the depths of the point forming a surface of the p-type which is usually already strongly degenerated (more than  $10^{15}$  electrons in  $1 \text{ cm}^2$ ). At such temperatures the boron is able to diffuse into the depths of the point in a few minutes at a distance on the order of several microns. The amount of boron which can "spoil" the original type of emitter is less than one thousandth of a mono-layer [6, 7]. The water vapors, the "carriers" of boron from the surface of the glass to the point, evidently play an important role.

The volt-ampere curves of EEE from thread-like silicon monocrystals were plotted by the authors of paper [8]. The emitters were heated in a vacuum at temperatures of about  $400^\circ\text{C}$ . At such a temperature boron diffusion can be disregarded, but the presence of an oxide film cannot be. The absence of emission patterns, the necessary criterion of a clean surface, decreases the value of the data obtained to a significant degree.

Fischer [9] notes that high temperature heating of silicon in a vacuum gives different volt-ampere curves which apparently may be related to a different degree of "poisoning" of the surface and of the volume of boron. His remark concerning the fact that the "configuration" of the emission pattern depends on the method of heat treatment and cooling of the emitter, deserves note.

Two characteristic types of volt-ampere curves of EEE from silicon (non-linear with some breaking in the area of large currents in the direction of decreasing current, and linear - without breaking) were observed by Perry [10]. Measurements were made under both static and pulse conditions. The author linked these two types of curves with the process of cleaning the surface of the points. The points from which the curves with breaking were obtained were cleaned by the method described in paper [1] giving a surface comparatively uncontami-

nated by boron without a dense stable p-layer. The points yielding a straight-line curve without breaking were cleaned by heating at temperatures of about 1600°K, so that boron could diffuse into the silicon forming a stable p-layer on the surface. The author suggests that the straight-line curves of EEE are similar to the volt-ampere curves of EEE from metals and are produced because of the strongly degenerated layer of the p-type which does not allow the field to penetrate inward and to distort the energy bands. The discontinuity in the nonlinear curve is linked with the penetration of the field.

In paper [11], to verify the role of boron diffusion into the silicon surface of the points, cleaning was done by high-temperature heating in a projector made of special glass not containing boron. Due to the fact that the whole vacuum apparatus was made of boron-containing pyrex glass, poisoning by boron occurred, but to a smaller degree; the p-layer turned out to be very much thinner and for one sample, it was found (from the thermo-e.m.f.) that approximately half of the surface remained n-type. Such points gave nonlinear volt-ampere curves, which enabled the author, using electron microphotography of the points, to some degree to compare the data obtained with the theoretical.

Allen [12] used a more complete method of cleaning the points - field desorption [13], which practically eliminates boron diffusion. However, he /64 could not clean the silicon surface by this method (for silicon, volt-ampere curves were obtained after high-temperature heating having the straight-line form), but for the germanium surface a straight-line curve was obtained in current ranges from  $1 \cdot 10^{-6}$  up to  $1 \cdot 10^{-11}$  A, in distinction to the volt-ampere curves with a break obtained in the paper [14], the authors of which did not observe a symmetrical emission pattern. However, as Stratton showed [4], a straight-line shape of the volt-ampere curves is possible under some exceptional

conditions (with a prevailing flow of EEE from the valence zone and in the case of linear distribution of the surface states). Numerical calculation [15], according to theory [3], gives an approximate straight-line relationship under some conditions.

Thus, to obtain reliable experimental data on EEE from silicon, it is necessary to produce emission patterns reflecting the structure of a monocrystal of chosen orientation. The emission pattern indicates that the surface is atomically clean in the sense of what is usually spoken of as the surface of the metallic point, giving a "pure" emission pattern. However, from the emission pattern of silicon it is impossible to determine the presence of very small amounts of boron (less than one-thousandth of a monolayer), located on the surface and diffusing into it. For this reason, it is necessary to be sure that the surface and the area adjacent to the surface is not "poisoned" by boron, which distorts the original electro-physical character of the reference monocrystal.

In the present work, we used the method of field desorption [13] to obtain emission patterns, which satisfies these demands and permits cleaning of the silicon point without prolonged heating at a high temperature. We consider that with the comparatively low temperatures and short duration of heating necessary for the initial degassing, this method allows one to disregard boron diffusion.

#### EXPERIMENTAL RESULTS

The stock of points was sharpened as in [1] from monocrystalline moldings of industrial silicon according to definite directions in the shape of a prong 1 (Figure 1) with an extension 2 at its apex. The lower part of this prong-

suspension was clamped to obtain a secure electrical contact with a special crystal holder 3 permitting heating of its upper part by passage of a current.

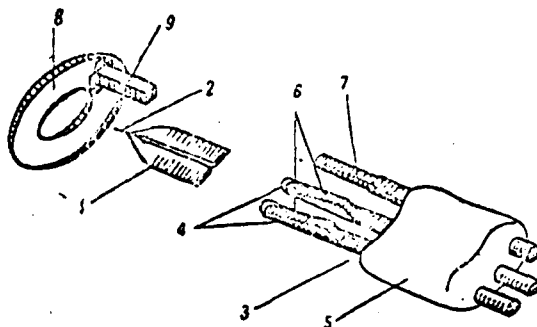


Figure 1

Since the cross section of the prong is smallest in the upper part, this part /65 can be heated to a high temperature while its lower part (together with the crystal holder) remains comparatively cool, which practically completely eliminates the possibility of contamination of the point with the crystal holder during heating. This method of heating has the advantage, in distinction to others, that alloys of metals with silicon which have very low melting points and consequently can heavily contaminate the surface of the point are not formed at the point of contact due to the low temperature.

The stocks were cut with a revolving ferro-nickel disk dampened with a suspension of a fine abrasive in turpentine. The extension 2 at the apex of the prong was ground in the shape of a cylinder with a diameter of the cross section of 0.8 mm and a length 1.5 mm, using a revolving disk (1400 rpm) dampened with a suspension of very fine synthetic corundum in SU oil or turpentine.

The overall dimensions of the stock (1 x 4, 8 x 15 mm) were selected so that it could be placed in the objective holder of an electron microscope (lens for gaseous medium).

After grinding of the cylinder the stock was etched in some chemical cor-

rosives to obtain "rounding" of the sharp edges and the cylindrical extension was etched to a point in a freshly prepared solution of 41.5% HF and "fuming"  $\text{HNO}_3$  in the proportion of 1:4.5. The stock, fastened in the crystal holder, was rotated around its axis (60 rpm) and lowered into an electrolyte bath. A platinum plate with an opening of 1.5 mm lying on the surface of the electrolyte served as the cathode. The focused ray of light was directed from the side onto the cylindrical part which was lowered into the electrolyte through this opening to hasten the process of etching and to obtain a smooth surface (illumination results in an increase in the concentration of current carriers in the surface layer). This was particularly expedient during etching of the points of n-type silicon, since in this case a decrease in the rectifying barrier on the silicon-electrolyte interface shows up particularly. The etching current was selected according to the type of the sample, its resistance, the temperature of the electrolyte and sample and the phase of etching within the limits of 100 to 0.5 ma. Inasmuch as the stock can be heavily contaminated by the etching current passing over it, increasing the degree of chemical etching of the electrolyte, it was blown out by a jet of air from a nozzle placed to the side. The required semiangle taper of the point was obtained by choosing the velocity of vertical travel of the point, carried out with the help of a micrometer screw. With optimal regulation of the etching, points were obtained with a rounded taper cross section, a semiangle taper of  $6-7^\circ$  and a radius of curvature of the apex of less than 1 micron. The length of the taper was usually 0.4-0.8 mm. A semiangle of the taper of more than  $7^\circ$  was not useful, since with field desorption the point is very strongly blunted. After etching the point and the crystal holder was washed in warm doubly distilled water, dried with filter paper and then washed in HF and absolute alcohol. The usual



time needed for preparing the point is 5-7 hours.

The crystal holder 3 (Figure 1) is two tungsten rods 35 mm long and 2 mm in diameter [4] fastened approximately in the middle with a glass bead 5. The rods were ground to half the diameter on a polishing wheel and the surfaces /66 obtained were carefully polished. The sharp edges were obliterated by grinding and electrolytic etching in a solution of alkali (electrolytic polishing formula). Nearer to the bead there were welded (across the platinum foil) tungsten terminals 6 prepared from tungsten wire with a diameter of 0.3 mm. The sharp ends of the terminals were sealed from above by the platinum foil welded to them, in order to prevent possible stray emissions. The sample placed between the smooth surface of the rods and the springy tungsten terminals, had a very secure electrical contact. At the side of the bead there was welded a third tungsten rod 7, on which was put a ring 8, covered inside and outside (made of annealed tantalum), with a holder 9. This ring is supported under the potential ground and prevents emission from the crystal holder.

Spherical projectors of the usual type with a conducting coating were used. To prevent emission from the "abutment" contacts during reverse connection of the voltage in desorption, corresponding notches were made at the place where these contacts are clamped to the conducting layer in the glass.

It was found that the process of soldering the shank in the projector and the heating for degassing of the glass system to 400°C have a very great effect on the thickness of the oxide film. Therefore, before placing the point in the projector, the latter, together with the manometer and the getter, were carefully degassed and unsoldered from the vacuum apparatus. The process of degassing also included a prolonged bombardment of the conducting coating and the lumiphore with electrons with an energy of up to 25-30 kev. After etching of

the point in the thus prepared apparatus for 10-15 min. the point was mounted and soldered onto the vacuum apparatus.

Further degassing of the glass was conducted with continuous control of the vacuum conditions. Evacuation was carried out with the usual mercury pumps, unsoldering -- at a pressure of  $\sim 10^{-9}$  mm mercury after degassing the glass at a temperature of  $\sim 400^\circ\text{C}$  for 8-10 hours. After atomization of the thin films of electron-bombarded silicon, titanium and tantalum, the pressure of the residual gases was less than  $10^{-10}$  mm of mercury according to readings of the Bayard-Alpert manometer. The points were heated for brief periods (20 sec.) at  $950\text{--}1350^\circ\text{K}$ . The brief bakings also decreased the probability of contamination of the point from the crystal holder. The temperature was controlled with an optical pyrometer with a correction for the appropriate coefficient of radiation of silicon [16] and the decrease in temperature along the taper of the point [12]. Inasmuch as the temperature relation of the resistance of silicon has a sharply nonlinear character [17], to establish the necessary current in the circuit of the point a choke coil with an adjustable saturation was used as a ballast resistance (Figure 2). During the initial heating, when there was an oxide film of great resistance between the silicon and the terminals, special high-voltage equipment for "breaking through" this film was used.

After this preliminary treatment of the surface, cleaning of the point by the field desorption method was carried out [13], allowing constant observation for changes in the emission pattern during desorption (in Figure 2 the position of the switches  $P_1P_2$  during desorption is at 1). It was established that the minimal possible temperature of the point for initial degassing before desorption is  $\sim 1350^\circ\text{K}$ . Heating at a lower temperature leads to the point often "collapsing" with the reverse field (apparently along a sort of sliding plane

of the crystal) and the radius of curvature increases very greatly.

The significant vacuum conditions were: the vacuum must be much better /67 than  $10^{-8}$  mm of mercury. This is connected, evidently, with the fact that the "coefficient of adhesion" of the residual gasses for silicon, which has a very great affinity for oxygen, is large.

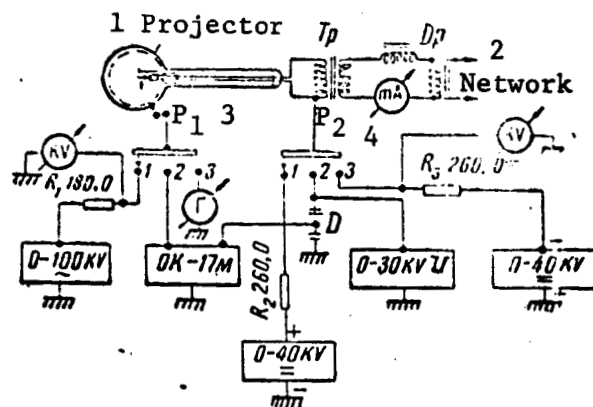


Figure 2

The reverse voltage, necessary to start desorption of silicon, exceeds by approximately five times the voltage necessary to obtain an emission current of the order of  $10^{-7}$  A.



Figure 3

The principal electrical circuit for desorption and measurements is presented in Figure 2. The position of the switches  $P_1P_2$  is: 1 - desorption; 2 - pulse measurements; 3 - measurements in a static system. Pulse measurements were carried out by the method described in paper [19]. During measurement of pulse currents of small magnitude, the broad-band amplifier of the OK-17M oscillograph was used with some modifications (at the input - a cathode follower with calibrated input resistances, rejector filters for suppressing stray /68 oscillations, etc.). In measuring large currents the signal was transmitted directly to the beam-deflection plate of the tube. The duration of voltage pulses was  $1.6 \times 10^{-6}$  sec. The error of the measurements was determined principally by the width of the beam on the screen of the oscillograph and was not more than 10%.

After preliminary degassing of the point at 1350°K, the emission pattern is randomly dispersed spots of various shapes. A similar pattern can be explained chiefly by the uneven oxide film at the apex of the point. Depending on the time of heating, crystallites can be formed from this film and give correspondingly small emission patterns with their symmetry.

After the first stage of field desorption the emission pattern is a more or less uniform luminescence in the center of the screen with very low-contrast (hardly discernible to the eye) image of the facets. Along the periphery the spots usually stop, and after heating at temperatures from 1000 to 1350°K they migrate to the center. Then the second stage of desorption is carried out, again brief heating, etc. as long as the entire field of the projector is occupied by the image of the emission pattern of the chosen symmetry. After brief heating (10-15 sec.) at temperatures of 900-1000°K for "smoothing" the surface of the point (since the surface of the point after desorption, in principle,

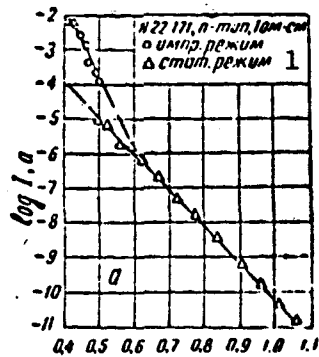
cannot be ideally smooth due to various physical properties of the facets having an effect on the amount of desorped material), the emission patterns have very great contrast (Figure 3, a-e). The contrast of the emission patterns of silicon greatly exceeds the contrast of the emission patterns of metals, for example, tungsten.

In the present work it was also proposed to investigate the temperature relation of EEE in as great a range of temperatures as possible. It turned out, however, that silicon is very easily "adjusted" by a field at temperatures of about 800°K (in paper [12] about 900°K) which narrowed the range of temperature measurements.

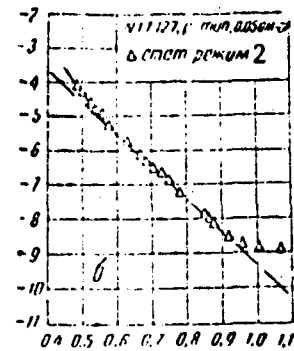
The volt-ampere curves for differently oriented monocrystals of silicon of the n- and p-type with a specific resistance of 0.05 - 72 ohm·cm were recorded. In the range of currents from  $5 \cdot 10^{-11}$  to  $1 \cdot 10^{-5}$  A. They turned out to be straight lines within the limits of experimental error. Pulse measurements up to currents of  $\sim 7 \cdot 10^{-2}$  A (at higher currents "collapse" of the point set in) gave a deflection of the volt-ampere curve in the direction of an increase in current, while a current under pulse conditions at the given voltage increased the current in the static system by at least one order of magnitude (Figure 4, a-d).

Figure 4 shows the volt-ampere curve in which the current at a temperature of the point of about 800°K (electrolytic polishing by the filament current) is designated by the points. The current at each point of the curve upon heating the point increased by no more than 15-20%.

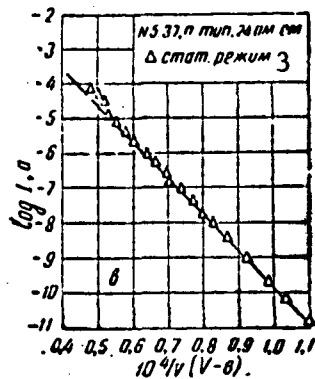
For silicon the maximal difference in the work function along the facets is less than 0.2 ev [20] and for tungsten it is a little larger [21]. Consequently, under similar conditions, the contrast of the emission pattern of



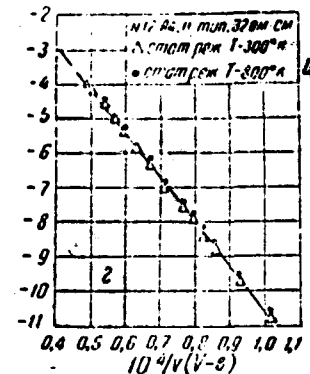
1. N 22.171, n-type,  
1 ohm·cm  
o pulse system  
Δ static system



2. N 17.127, p-type,  
0.05 ohm·cm  
Δ static system



3. N 5.37, n-type,  
24 ohm·cm  
Δ static system



4. N 12.84, n-type,  
32 ohm·cm  
Δ static system  
T 300°K  
o static system  
T 800°K

Figure 4

silicon must be less than the contrast of the tungsten pattern. The observed high contrast of the emission patterns (Figure 3) must be ascribed to the large change in the local curvature of the silicon surface. Only the fact that heating to temperatures of about 900°K for a few seconds can occasion such a /69 strong development of peaks and levels (for decreasing the free surface energy), although the energy of surface migration is 2 ev [12] and differs little from the energy of surface migration of tungsten [21], causes doubt.

It is possible that a change in the density of the surface states (distribution of the Tammovskiy surface states) along crystallographic directions [22] which is apparently possible at densities of the surface states exceeding  $5 \times 10^3$  in  $1 \text{ cm}^2$ , has an effect on the contrast of the emission patterns. One may assume a large density of the surface states for the following reasons. Since, for silicon without surface states, a field on the order of  $10^6 \text{ v/cm}$  distorts the zones by a magnitude on the order of a tenth of an electron volt, that is, on the order of the maximal difference in the output along the facets of silicon [2, 3], for two neighboring regions with a difference in the work functions  $\Delta F$  which is also on the order of a tenth of an electron volt, their work functions will be changed very little in such a distance  $d$  that the force of the field  $\frac{\Delta F}{d}$  will be sufficient to distort the energy zones to a magnitude comparable with  $\Delta F$ . At  $\Delta F = 0.2 \text{ ev}$  the necessary field is  $\sim 10^6 \text{ v/cm}$  and  $d$  is  $\sim 10^{-7} \text{ cm}$ , that is, in this case the emission pattern must be more or less light and dark spots with very smooth transitions among them; even simply a uniform illumination of the screen is possible. Only the surface states can screen these "fields of spots" and in this way prevent distortion of the energy zones. /70

Such an explanation also raises some doubt, since with large magnitudes of the field strength the energy barrier of the surface states, generally speaking, is already suppressed and the patterns are observed with almost undecreasing contrast. Some decrease in the contrast observed in this case may be attributed to the illumination of the dark places of the pattern by dispersed light from the brighter sections.

In Figure 5 a-c the volt-ampere curves obtained in papers [10, 11] are presented for comparison.

In the range of currents which we investigated one may expect a discon-

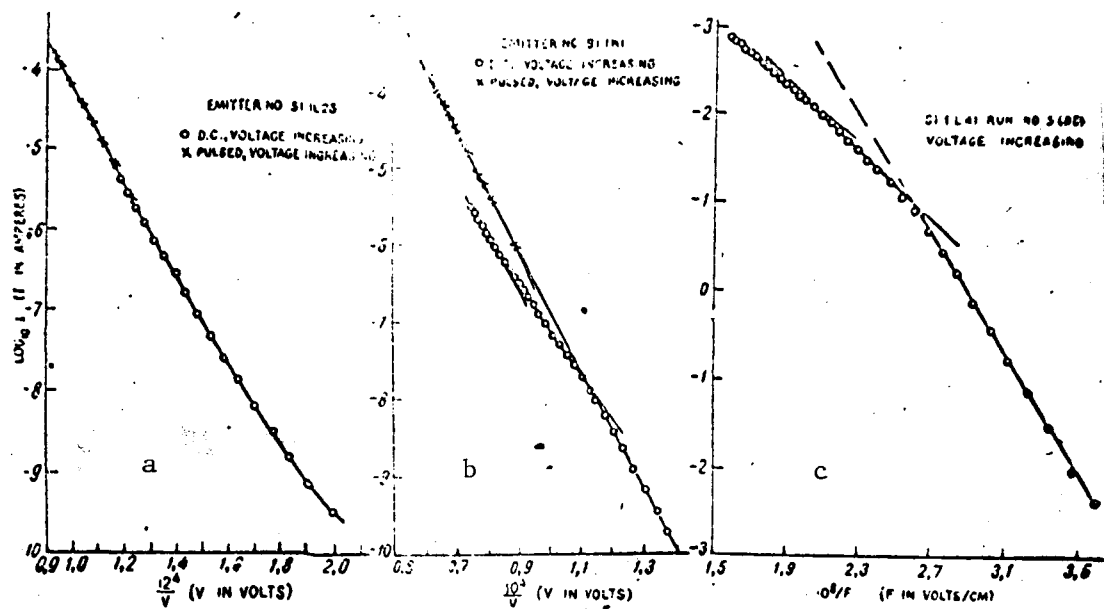


Figure 5

tinuity in the volt-ampere curves which is connected with the penetration of the field into the "typical" semiconductor [2-4]. Less probable is the approximate straight-line shape of the curve, possible for some exceptional cases (linear distribution of the surface states, predominant emission from the valence zone, etc.) [4, 15].

In not one of the volt-ampere curves which we obtained, within the limits of experimental error, was a similar discontinuity observed. On the contrary, the volt-ampere curves were bent in the direction opposite to the increase in current. Evidently, this shape of the volt-ampere curves can be explained by the fact that with such fields the emission has a non-equilibrium character [23]. A significant electrical field within the emitter leads to "discontinuity" of the electron gas in comparison with the temperature grid and a dependence of the electron concentration of the conductivity on this field.

Volt-ampere curves similar to ours were obtained for some semiconductor compounds [24]. Such an effect, evidently, overlaps in this case the simple



"strong" penetration of the field into the semiconductor. However, as was noted [25], in some cases they did not succeed in producing superheating of the electron gas; the volt-ampere curves either depart from a straight-line /71 shape in the direction of a decrease in current, as should be expected with a strong penetration of the field, or remain straight-line during the simultaneous action of the strong penetration and superheating.

We note that straight-line curves must be obtained in the case of strong degeneration of the surface (approximation to metals). In this case, an increase in current may be explained by possible effects linked with the initial heating of the point by the Joule effect due to the passage of the emission current along the body of the point. Such initial heating is possible also for a non-degenerated surface. Since, in our case, we consider that degeneration does not occur, the explanation of the increase in current with large intensities of "superheating" of the electron gas seems to us completely plausible.

A "break" in the volt-ampere curve between the pulse points and the points of the static system (Figure 4) is not explained by the author of paper [10] (Figure 5). It may, evidently, be supposed that in this case we are dealing with some sort of relaxation processes linked with the surface of the semiconductor.

#### CONCLUSIONS

1. To obtain a clean surface of silicon emitters the method of field desorption was used, eliminating the necessity for intense heating of the point and decreasing the probability of boron diffusion, which permitted a comparison (although only qualitative) of the experimental data with the theoretical.

2. The volt-ampere curves of EEE obtained from silicon for different orientations of the monocrystals under static and pulse conditions are straight, deflecting in the direction of an increase in current.

3. To explain the behavior of the curve in the region of large currents, the model of "initial heating" of the electron gas is drawn upon.

4. The temperature dependence of EEE from silicon in this current range is a constant "addition" at each point of the curve of 15-20% at a temperature of about 800°K.

I consider it my obligation to express gratitude to Professor G. N. Shuppe for guidance in the present work.

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